



TITLE:

Nitration of Desoxybenzoin

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ABSTRACTS

Effects of leaching conditions on the extraction of chromium were studied.

1. Size of ore, 2. Leaching time, 3. Amount of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ added, 4. Leaching temperature, and 5. Amount of charge.

Summary of Result : Results obtained are summarized in Table 1, which shows the optimum conditions for extraction of chromium.

If the acid concentration was increased up to 60%, insoluble brownish-yellow precipitate was formed in the presence of $(\text{HN}_4)_2\text{Cr}_2\text{O}_7$ in both cases of leaching.

Reaction of *n*-Hexyl Bromide with Potassium Fluoride in Several Glycols

Hisao KITANO and Ken-ichi FUKUI

(Kodama Laboratory)

J. Chem. Soc. Japan. Ind. Chem. Sec. (Kōgyō Kagaku Zasshi), **60**, 272 (1957)

Reactions of *n*-hexyl bromide with potassium fluoride in isomeric propanediols and butanediols are studied. *n*-Hexylfluoride is obtained in high yields by the use of such glycols that have two adjacent hydroxy groups in the molecule. Two geometrical isomers of 1,2-cyclohexanediols are used as the solvent. The yield of *n*-hexyl fluoride is ca. 30% in the *trans* isomer, whereas it's only 2% in the *cis* isomer.

Nitration of Desoxybenzoin

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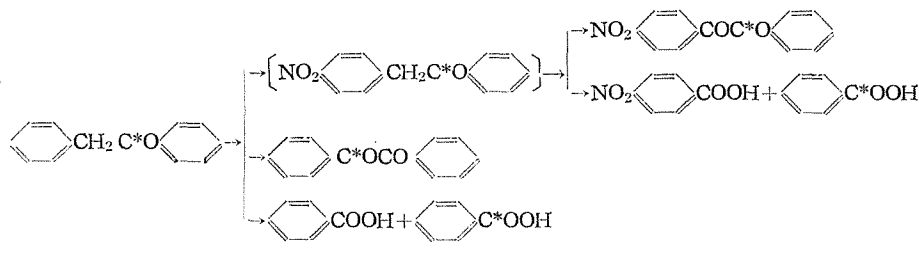
J. Org. Chem., **22**, 288 (1957)

The reaction routes of desoxybenzoin with nitric acid ($d=1.30$) were studied by using C^{14} -tracer technique. By the nitration of desoxybenzoin-carbonyl- C^{14} (I) ($12.95\mu\text{c}/\text{m.mole}$) there were obtained *p*-nitrobenzil-carbonyl- C^{14} (II) ($12.92\mu\text{c}/\text{m.mole}$), benzil-carbonyl- C^{14} (III) ($12.96\mu\text{c}/\text{m.mole}$), inactive *p*-nitro-benzoic acid (IV) and benzoic acid-carboxyl- C^{14} (V) ($11.29\mu\text{c}/\text{m.mole}$). When treated with alcoholic potassium hydroxide, II decomposed into inactive *p,p'*-azoxydibenzoic acid, inactive *p*-nitrobenzoic acid and benzoic acid-carboxyl- C^{14} ($12.96\mu\text{c}/\text{m.mole}$). These facts indicate that the nitration occurs at the *para* position to the methylene group of I.

The non-labeled specimens of *p*-nitrodesoxybenzoin, *p*-nitrobenzil, and benzil were treated with the nitric acid, respectively. *p*-Nitrodesoxybenzoin gave benzoic acid, *p*-nitrobenzoic acid, and *p*-nitrobenzil. Benzil and *p*-nitrobenzil, however, were resistant to nitration and oxydation, and were recovered without loss. The specific activity of V is comparatively lower than the theoretical value. These results would lead to the following conclusions. In the action of the nitric acid on desoxybenzoin-carbonyl- C^{14} , the *p*-nitrodesoxybenzoin-carbonyl- C^{14} is formed as an intermediate, and its methylene group is oxidized to *p*-nitrobenzil-carbonyl- C^{14} . While oxidative disruption of the same intermediate gives benzoic acid-carboxyl- C^{14}

ABSTRACTS

and inactive *p*-nitrobenzoic acid. A similar oxidation and oxidative disruption prior to the nitration of desoxybenzoin-carbonyl-C¹⁴ also take place and give benzil-carbonyl-C¹⁴, benzoic acid-carboxyl-C¹⁴ and inactive benzoic acid. The essential reaction routes are shown as follows.



Studies on Condensation Products of Chlorinated Phenols with Chloral. (I)

The Structure of Condensation Product of 2,4-Dichlorophenol or 2,4-Dichloroanisole with Chloral

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Scientific Insect Control (Botyu-Kagaku), **22**, 231 (1957)

In recent paper, Riemschneider [*J. Am. Chem. Soc.*, **76**, 4853 (1952)] obtained a compound II, 154°, by methylating condensation product (I) of 2,4-dichlorophenol with chloral, and another compound V, mp. 160°, by condensing 2,4-dichloroanisole with chloral. He proposed (1) these two compounds were stereoisomers of 1,1-bis-(2'-methoxy-3',5'-dichlorophenyl)-2, 2, 2-trichloroethane resulting from the restricted rotation of benzene rings, and (2) the dichloroethylene compounds III, mp. 166°, and VI, mp. 157°, obtained by dehydrochlorination of compounds II and V, respectively were also the same type stereoisomers.

This study was undertaken to ascertain the above results and obtained the following conclusion. To a mixture of above 1,1-bis-(x'-methoxy-y', z'-dichlorophenyl)-2, 2, 2-trichloroethane (compound II or V) and diethylene glycol was added a concentrated potassium hydroxide solution, and then the mixture was refluxed at 160-70° for 5 hours. Bis-(x-hydroxy-y, z-dichlorophenyl)-methane (IV), mp. 167.5-68.5°, was obtained from compound II through hydrolysis, decarboxylation and following demethylation. Compound IV was not identical with the corresponding compound VII, mp. 152.5-53.5°, obtained from compound V. Compound IV was also prepared by condensing 3, 4-dichlorophenol with paraformaldehyde. Compound IV was then dechlorinated to bis-(2-hydroxyphenyl)-methane, mp. 117-18°, with sodium in liquid ammonia. From the above, it was confirmed that the structure of compound II is 1,1-bis-(2'-methoxy-3', 5'-dichlorophenyl)-2, 2, 2-trichloroethane which was identical with the structure proposed by Riemschneider.

On the other hand, a compound, mp. 96-97°, which was obtained by the same procedure from compound VII, was identical with bis-(3-hydroxyphenyl)-methane